Acta Societatis Botanicorum Poloniae

DOI: 10.5586/asbp.3600

Publication history
Received: 2018-06-28
Accepted: 2018-11-09
Published: 2018-12-31

Handling editor
Bronisław Wojtuń, Faculty of Biological Sciences, University of Wrocław, Poland

Authors' contributions
MHW, PWP: research designing; MHW, SLK, MO: fieldwork; PN: laboratory analyses; PWP: statistical analyses; MHW, PWP, MO: manuscript writing

Funding
The specimens from 2008 were collected within the Polish Research Project N N305 035634 of the Ministry of Science and Higher Education. The contribution made by PWP received financial support from the statutory fund of the Institute of Botany of the Jagiellonian University (K/DSC/005528).

Competing interests
No competing interests have been declared.

Citation
Węgrzyn MH, Wietrzyk-Pełka P, Nicia P, Lehmann-Konera S, Olech M. Short-term monitoring of Arctic trace metal contamination based on *Cetrariella delisei* bioindicator in Svalbard. Acta Soc Bot Pol. 2018;87(4):3600. https://doi.org/10.5586/asbp.3600

ORIGINAL RESEARCH PAPER

Short-term monitoring of Arctic trace metal contamination based on *Cetrariella delisei* bioindicator in Svalbard

Michał Hubert Wegrzyn[1]*, Paulina Wietrzyk-Pełka[1], Paweł Nicia[2], Sara Lehmann-Konera[3], Maria Olech[1]

[1] Professor Z. Czeppe Department of Polar Research and Documentation, Institute of Botany, Jagiellonian University, Gronostajowa 3, 30-387 Krakow, Poland
[2] Department of Soil Science and Soil Protection, University of Agriculture in Krakow, Mickiewicza 21, 31-120 Krakow, Poland
[3] Department of Analytical Chemistry, Faculty of Chemistry, University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

* Corresponding author. Email: michal.wegrzyn@uj.edu.pl

Abstract
This study focuses on short-term monitoring of trace metals in the Svalbard archipelago. Short-term studies using lichen bioindicators are important because temporary changes in lichen trace metal levels are mainly dependent on air pollutants. Here, we investigated temporal and spatial differences in the content of trace metals such as Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn measured in the lichen thalli of *Cetrariella delisei*. The temporal aspect was studied in the marine plain of Calypsostranda between 1988 and 2016 and that of Hornsundneset between 1985 and 2008. The spatial aspect was studied between Hornsundneset in 1985 and Calypsostranda in 1988 as well as between Hornsundneset in 2008 and Calypsostranda in 2016. The results revealed an increase in the concentration of Cr, Mn, Ni, and Co for both the aspects, while a decrease in the contents of Cu, Cd, and Mo was observed. Pb content varied, as Pb level increased with time in Hornsundneset but decreased in Calypsostranda. The Zn content showed no significant changes in both temporal and spatial aspects.

Keywords
lichens; heavy metals; potential toxic metals; spatial and temporal trends; Spitsbergen

Introduction

The distribution of trace metals among marine and terrestrial ecosystems in polar regions is dynamic and is thought to be driven by multiple synergic processes. The sources of trace metals have both natural and anthropogenic characters [1]. The anthropogenic sources of pollutants in the Arctic region are related to the long-distance transport of toxic substances from lower latitudes [2]. The transport of new pollutants may increase the levels of natural trace metals resulting from local geology [3]. The accumulation of trace metals may occur directly through atmospheric deposition [4,5] and indirectly through the influence of marine aerosols, windblown dust, and water from melting snow and glaciers [2,6–10].

Regardless of their origin, trace metals accumulate in terrestrial ecosystems in the substrate and are absorbed thereafter by vascular plants and bryophytes [11]. The lichens accumulate trace metals directly from air and indirectly from substrate [11]. Given their ability to absorb pollutants from the air [12,13], lichens are widely used as bioindicators of trace metal pollution all over the world [1,8].

Climate changes observed in the Arctic region during last 30 years have significantly affected the tundra vegetation in Svalbard archipelago [14,15]. These changes coupled with increasing herbivore pressures have led to a noticeable decline in the number of species of terricolous, fruticose lichens such as those from the genera *Cladonia* and *Cetraria* s. l. [14,16]. In the past, these genera had broad geographical ranges and were commonly present throughout the archipelago. As these genera have been the major components of the high Arctic tundra vegetation, they were frequently used as trace metal bioindicators [2,8,17–20]. The studies involving lichens as biological indicators of trace metal contamination have mainly been conducted in the regions of Bellsund [21–23] and Hornsund [7,13,24,25]. The data of these reports have been used for comparative studies that are necessary to achieve the objectives of an AMAP (The Arctic Monitoring Assessment Program) initiative [1]. One of the assumptions of this program is the assessment of temporal trace metal trend that provide essential information for decision makers connected with science-based policy decision on contaminants in the Arctic environment [1]. Short-term data (i.e., <30 years) are developed on the basis of the bioindicator studies (including lichens) and cover information from previous 1–3 decades. These data illustrate how trace metal contents have changed in time and indicate their trends in the future. Short-term studies that use lichen bioindicators are also important because the changes in the levels of trace metals in lichens are not subject to strong fluctuations, as in the case of measurements of air contamination [26].

At present, the lack of the availability of the lichen material for comparative research poses a problem. Species of macrolichens that form large surface thalli, such as *Flavocetraria cucullata* (Bellardi) Kärnefelt & A. Thell, *F. nivalis* (L.) Kärnefelt & A. Thell, *Cladonia mitis* Sandst., and *Thamnolia vermicularis* (Sw.) Schaer., collected in the 1980s and 1990s on the coastal terrains of NW Wedel Jarlsberg Land and NW Sørkapp Land, now failed to occur in these regions owing to the heavy grazing activity of reindeer [13,14,16]. Therefore, it is very difficult to repeat previous studies conducted on these species and compare the results with the original data.

Until now, the only short-term study for the period of 8 years has been performed on Calypsostranda plain [23] in the NW Wedel Jarlsberg Land; however, the results were not compared based on individual years but only averaged to have a better representation of the whole region. Thus, the short-term data sets from this part of the Arctic region are very poor.

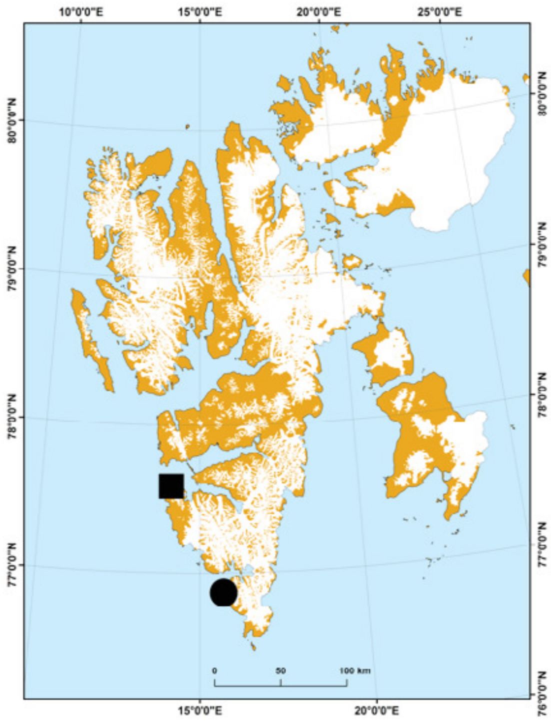

Fig. 1 Localities of *Cetrariella delisei* samples on Svalbard black square – Calypsostranda, NW Wedel Jarlsberg Land; black circle – Hornsundneset, NW Sørkapp Land (© Norwegian Polar Institute 2018, http://www.npolar.no).

Within the monitoring survey, nine trace metals (Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn) were measured in the thalli of *Cetrariella delisei* (Bory ex Schaer.) Kärnefelt & A. Thell. Here, we aim to investigate the spatial and temporal differences in the contents of these trace metals. The temporal aspect was studied for the marine plain of Calypsostranda between 1988 and 2016 as well as for the marine plain of Hornsundneset between 1985 and 2008. The spatial aspect was studied between Hornsundneset in 1985 and Calypsostranda in 1988 as well as between Hornsundneset in 2008 and Calypsostranda in 2016. The hypothesis set was as follows: the content of the studied trace metals in lichen thalli collected in Hornsundneset in 2008 and Calypsostranda in 2016 is lower than that in the samples collected in Hornsundneset in 1985 and in Calypsostranda in 1988.

Material and methods

Herbal material collection

The study included the herbarium specimens of *C. delisei* lichen that were collected in Calypsostranda marine plains (NW Wedel Jarlsberg Land, Spitsbergen) and Hornsundneset marine plains (NW Sørkapp Land, Spitsbergen) by various researchers (Fig. 1 and Tab. 1). Calypsostranda area shows rocks of tylloid in alternation with other rocks from sedimentary to low-grade

Tab. 1 List of localities where the samples of *Cetrariella delisei* were collected.

No.	Region	Localities	Collected by	Date
1	Wedel Jarlsberg Land	Calypsostranda	F. Święs	1988
2	Wedel Jarlsberg Land	Calypsostranda	S. Lehman-Konera	2016
3	Sørkapp Land	Hornsundneset	M. Olech	1985
4	Sørkapp Land	Hornsundneset	M. Węgrzyn	2008

metamorphic type, while Hornsundneset marine plain comprises rocks of sandstone, siltstone, and shale. For laboratory analysis, minimal quantities of lichen thalli were obtained from herbarium specimens that were stored in lichenological envelopes in the Herbarium of the Institute of Botany in the Jagiellonian University (KRA).

Laboratory analyses

Two replicates of 3 g from each lichen sample were homogenized and dried at 105°C, followed by mineralization and extraction in aqua regia for 16 h, according to a previously described method [27]. After extraction, the samples were digested at 130°C for 2 h, filtered, and mixed in 0.5 mol nitric acid (HNO_3) in 100-mL flasks. The levels of Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn in each sample were detected in four replications with the Perkin Elmer Optima 7300 DV optical emission spectrometer using the inductively coupled plasma-optical emission. The plasma gas flow rate was 15 dm^3 min^{-1}, the external gas flow rate was 0.2 dm^3 min^{-1}, and the nebulizing gas flow rate was 0.6 dm^3 min^{-1}. Calibration was carried out using a certified reference material ERM-CD 281.

Statistical analyses

Levene's test was performed to assess the equality of variances and Shapiro–Wilk test was applied to assess normality. Wilcoxon test was used to investigate the differences in element contents in *C. delisei* thalli in temporal aspect between specimens collected in 1985 and 2008 in Hornsundneset as well as between those collected in 1988 and 2016 in Calypsostranda. Mann–Whitney *U* test was applied to test the spatial differences in element contents measured in lichen thalli collected in 2008 in Hornsundneset and 2016 in Calypsostranda as well as to analyze the difference between the data from 1985 and 1988. Statistical analyses were carried out using Statistica 10 software [28].

Results

Nine trace metals (Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn) were investigated in terms of their contents in the thalli of *C. delisei* collected in Calypsostranda in 1988 and 2016 as well as in Hornsundneset in 1985 and 2008 (Fig. 2).

The differences in the temporal changes in the trace metal contents were significant between Hornsundneset in 1985 and 2008 for all the studied elements (Tab. 2). For Calypsostranda in 1988 and 2016, the differences in the changes in the element content were significant for the following trace metals: Co, Cr, Cu, Mn, Ni, and Pb (Tab. 2). However, the differences were not significant for the change in the content of Cd, Mo, and Zn between Calypsostranda in 1988 and 2016 (Tab. 2). The differences in spatial changes in the trace metal contents measured in lichen thalli were not confirmed for all the studied elements (Tab. 3). The differences were significant between Hornsundneset in 1985 and Calypsostranda in 1988 for following trace metals: Cd, Co, Cr, Mn, Ni, and Pb. The content of Co, Cr, Mn, and Pb showed significant variation between Hornsundneset in 2008 and Calypsostranda in 2016 (Tab. 3).

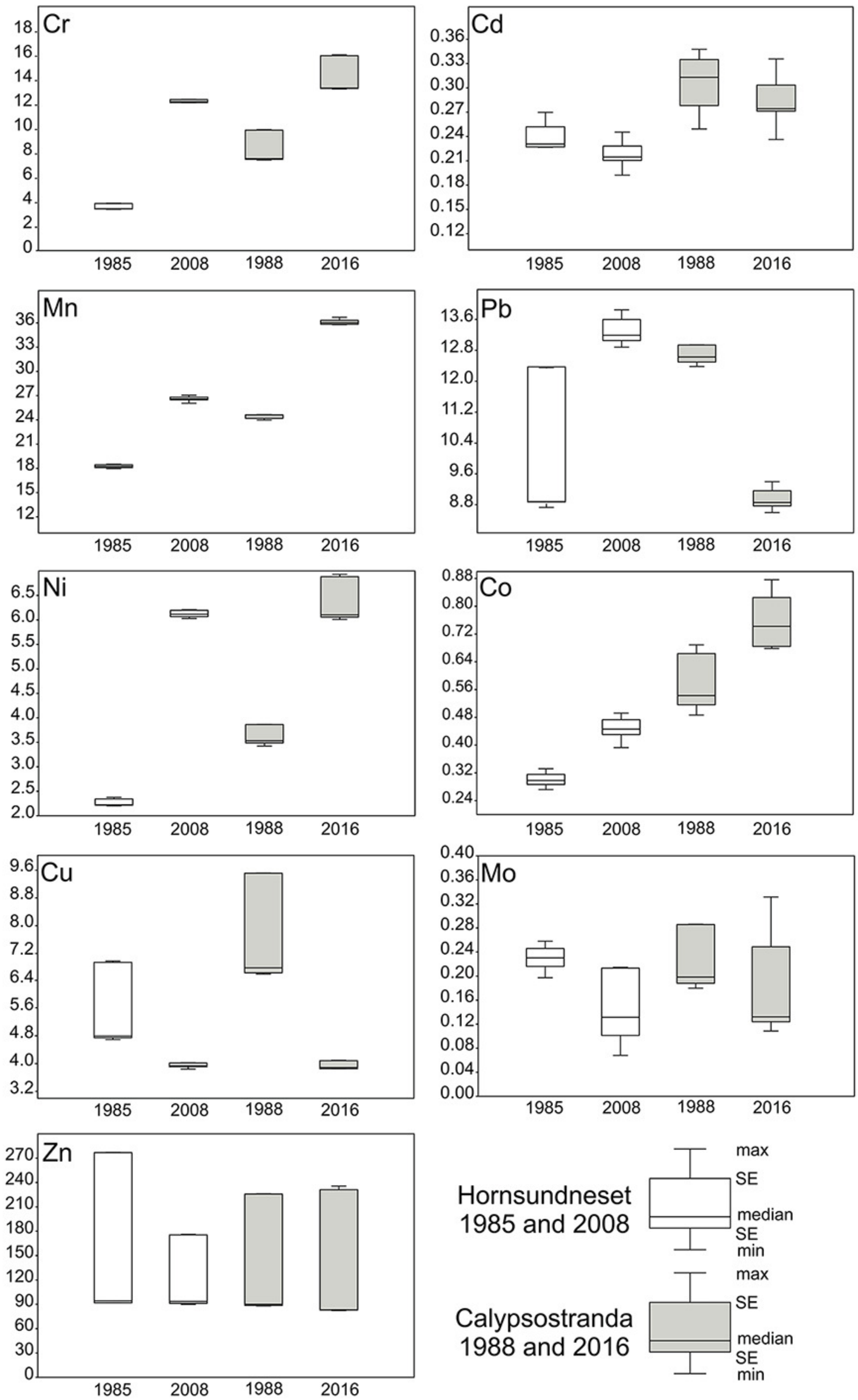

Fig. 2 The contents of trace metals (mg kg^{-1}) measured in the thalli of *C. delisei* collected in Calypsostranda in 1988 and 2016 and Hornsundneset in 1985 and 2008.

Tab. 2 The results of Wilcoxon test showing temporal changes in Hornsundneset between 1985 ($N = 8$) and 2008 ($N = 8$) and Calypsostranda between 1988 ($N = 8$) and 2016 ($N = 8$), $p = 0.05$.

	Hornsundneset 1985 vs. Hornsundneset 2008			Calypsostranda 1988 vs. Calypsostranda 2016		
Element	T	Z	p	T	Z	p
Cd	4.0	1.96	**0.04995**	9.0	1.26	0.2076
Co	0.0	2.521	**0.01172**	1.0	2.38	**0.01729**
Cr	0.0	2.521	**0.01172**	0.0	2.521	**0.01172**
Cu	0.0	2.521	**0.01172**	0.0	2.521	**0.01172**
Mn	0.0	2.521	**0.01172**	0.0	2.521	**0.01172**
Mo	2.0	2.24	**0.02506**	10.0	1.12	0.2626
Ni	0.0	2.521	**0.01172**	0.0	2.521	**0.01172**
Pb	0.0	2.521	**0.01172**	0.0	2.521	**0.01172**
Zn	32.0	2.521	**0.01172**	14.0	0.5601	0.5754

The significant differences are in bold.

Tab. 3 The results of Mann–Whitney *U* test showing spatial changes between Calypsostranda in 1988 ($N = 8$) and Hornsundneset in 1985 ($N = 8$) and between Calypsostranda in 2016 ($N = 8$) and Hornsundneset in 2008 ($N = 8$), $p = 0.05$.

	Hornsundneset 1985 vs. Calypsostranda 1988			Hornsundneset 2008 vs. Calypsostranda 2016		
Element	U	Z	p	U	Z	p
Cd	3.0	2.993	**0.00276**	1.0	−3.203	**0.00136**
Co	0.0	3.308	**0.00094**	0.0	−3.308	**0.00094**
Cr	0.0	3.308	**0.00094**	0.0	−3.308	**0.00094**
Cu	16.0	1.628	0.10356	28.0	−0.368	0.71319
Mn	0.0	3.308	**0.00094**	0.0	−3.308	**0.00094**
Mo	23.0	−0.893	0.37203	20.0	−1.208	0.22715
Ni	0.0	3.308	**0.00094**	27.0	−0.473	0.63650
Pb	0.0	3.308	**0.00094**	0.0	3.308	**0.00094**
Zn	16.0	−1.628	0.10356	32.0	0.053	0.95812

The significant differences are in bold.

Discussion

Studies concerning short-term trends in trace metal contents measured in lichens thalli have not been conducted in Svalbard. This is probably owing to the lack of historical herbal materials that may be used for comparative research. The results show that the temporal changes in the trace metal contents in *C. delisei* thalli were not identical for all elements (Fig. 2). For the four trace elements Co, Cr, Mn, and Ni, an increase in the concentration was observed for both the studied areas (Fig. 2). Three elements Cd, Cu, and Mo showed a decrease in their concentrations (Fig. 2); however, the difference was significant only for Cu (Tab. 2). For Pb, the trends observed in both the areas were different; Pb concentration increased in Hornsundneset but decreased in Calypsostranda (Fig. 2). Zn contents in both temporal and spatial aspects showed no significant changes (Fig. 2). The hypothesis set herein was not confirmed by the observed results (Fig. 2 and Tab. 2), as not all trace metals showed a decrease in levels in the lichen thalli during 23 years from 1985 to 2008 for Hornsundneset and 28 years from 1988 to 2016 for Calypsostranda. It is difficult to predict the factors that caused the decrease in the levels of some elements with the simultaneous increase in the levels of other elements in a situation, wherein air pollution monitoring surveys clearly indicated decline in trace element concentrations [29]. The attempt to answer is a part of a long-year discussion based on numerous investigations that evaluate the problem of the accumulation of pollutants by lichens under various aspects. The most important ones are discussed below.

Lichens are slow-growing and long-living symbiotic organisms that produce thalli, which lack roots or waxy cuticles and rely on an atmospheric input of mineral nutrients. These features of lichens combined with their wide occurrence in Arctic areas make them good bioindicators of air pollution [30,31]. Despite these anatomic and morphological features, numerous studies have indicated the occurrence of a process of selective accumulation of individual elements within the thallus [32]. This phenomenon exists because the accumulation of trace elements occurs both at the intracellular and extracellular (in the spaces between the cells of lichen thallus) regions. In the thalli of lichens, the cations of trace elements bind to the extracellular anionic exchange sites that are located in the cell wall and plasma membrane surfaces [33,34]. Lichens as bioindicators have an advantage over other organisms, owing to their capacity to retain high amounts of contaminants in particulate forms in large intercellular spaces [35,36]. Studies have suggested that these cell wall-bound elements are readily exchangeable; therefore, extracellular amounts and proportions reflect the recent environmental input [37]. Furthermore, the accumulation of trace elements by extracellular secondary metabolites is a permanent phenomenon, which often leads to morphological changes in the thallus at high concentrations of toxic elements [38]. Oxalates considered as one of the most effective extracellular mechanisms of heavy metal detoxification are widely distributed in lichens [39–41]. In the Arctic areas, such morphological changes fail to occur because of the low levels of contamination; however, the accumulation of the selected trace elements occurs in the intercell spaces in the form of permanent complexes. Total trace elements in the thallus of lichens are the most important fractions because the intracellular fraction accounts for only about 5% of the total content [42].

Trace element concentration in lichens is a dynamic process. Short-term research on the effects of excess metals showed that the lichens soaked into trace metal solutions accumulated elements quickly, in most cases within a few hours. In the case of Cu, maximum accumulation was observed after 3 to 6 h [43]. Transplantation studies showed that most lichens respond to the changes in the atmospheric pollutants within a few months, while the residence time of many elements in lichen thalli is 2 to 5 years [44]. In transplantation studies of lichen thalli [44], the initial levels of trace metals were determined and the changes in the accumulation of elements in the thallus at a given time were monitored. Thus, the heavy metal content of lichens may increase as a function of time; however, the situation is much more complicated. In fact, the content of several trace elements in the transplanted lichens increased, while that of other elements decreased during the study period [36]. This observation may explain that the contents of these elements are, at least in part, controlled by physiological processes and turnover mechanisms [36].

In relation to Calypsostranda, Jóźwik [23] conducted numerous studies on trace metal levels in lichens between 1987 and 1995. In these studies, several species of lichens were used as bioindicators, including *C. delisei*. Studies in Calypsostranda area carried out in 1987 by Jóźwik [22] highlighted the differences between trace metal contents obtained in the currently analyzed samples of *C. delisei* from 1988. The samples from 1987 showed the following values: Mn, 5.82 ±0.42 mg kg^{-1}; Cu, 3.58 ±0.25 mg kg^{-1}; and Zn, 60.8 ±5.58 mg kg^{-1} [22]. These values are four and two times lower than those reported in the present study (Fig. 2). However, the values of Cd (0.96 ±0.01 mg kg^{-1}) and Pb (25.52 ±0.03 mg kg^{-1}) were twice as high as those reported in the present study (Fig. 2). The method of mineralization of lichen samples is probably responsible for the observed differences. The lichen material was mineralized in a mixture of nitric acid (63%) and perchloric acid (60%) at 7:1 ratio [22], which is different compared to the mineralization process carried out using aqua regia, as performed in the laboratory analysis in the present study. There is no universal dissolution method, but the results of the methodological study [45], wherein the plant material was thoroughly washed with water with subsequent ashing at 550°C and digestion with a mixture of HNO_3:H_2SO_4 (2:1), suggest that the method employed in the present study is suitable for the quantitative determination of trace elements in vegetation. The results [44] of the trace element contents in a standardized plant material show that the use of aqua regia in relation to Cd and Pb provides almost twice lower content than that obtained using a mixture of nitric acid (63%) and perchloric acid (60%).

Despite differences in the compared results from 1987 and 1988, the obtained results are similar except for Cu, as Cu content in 2016 was similar to that reported by Jóźwik [22].

In Hornsundneset in Sørkapp Land area, the first study on the evaluation of the level of contamination of trace metals in the lichen and bryophytes was carried out in 2013 [13]. In comparison to the obtained results, Ni, Cr, and Cu had similar values, while Mn and Zn had about five times higher values. Pb value was three times higher, while Cd concentration was ten times higher. The lichen materials collected in 2008 and used in the present study were obtained from the coast approximately 300 m away from the shoreline, while the material used for the research in 2013 [13] was collected from the slopes of the Hohenlohefjellet mountain at a distance of about 1.4 km from shoreline. The impact of the marine aerosol on lichens growing near the shoreline may have affected the levels of trace metals, mainly Cd and Pb [11]. Similar impact of marine aerosols on lichens has been reported while evaluating the accumulation of trace metals in a research conducted in the Kaffiøyra plain [11].

Almost all of the studied elements, except Mo and Zn, showed higher concentrations in Calypsostranda region in 1988 than in Hornsundneset region in 1985 as well as between these regions in 2016 and 2008 (Fig. 2). This observation may be associated with the influence of mining activity in the northwestern part of Wedel Jarlsberg Land [46] before the establishment of the Sør-Spitsbergen National Park. Thus, in this area, the source of trace metals accumulated in lichens seems to be not only the long-distance transport of pollutants with air masses but also the human activities. Throughout Sørkapp Land, hunting was the only form of human activity before the establishment of Sør-Spitsbergen National Park. As a result, the only source of trace metals in lichen thalli is the long-distance transport of pollutants and natural geological background [13].

With regard to the other regions of the Arctic, our research shows that the accumulation of trace metals in a particular year in lichen thalli is not the same for all elements. This is important during the comparison of the data on the measurements of the trace metal contamination from air. For instance, short-term studies conducted at meteorological station Alert, Ellesmere Island station in Canadian Arctic [26], showed decreasing trends of concentration for Cu, Mn, Pb, and Zn in the years 1980–1995. While other Zeppelin Mountain station close to Ny-Ålesund, Svalbard [29], had not recorded any significant temporary trends in concentrations of Pb, Cd, Cu, Zn, Cr, Ni, Co, and Mn from 1994–2002. The results in this study do not correlate with our values of the trace metal recorded in lichen thalli, as the values of the four elements increased and similar trends were reported for only one element (Fig. 2).

In the Arctic region, the only temporal data available for lichens were from Nuuk (Greenland) where the samples of *F. nivalis* were collected in 1994 and 1999 [1,8]. The present study is the first report that analyzed short-term level of trace metals using lichens as bioindicators in Svalbard. Reducing pollutant emission contributes to the improvement in the conditions in the Arctic region. The monitoring of trace metal pollutants in air is very important; however, the response of biotic elements to the changes in the pollutants may only be assessed using the tried and tested bioindicators. Lichens, including, *C. delisei*, are good sources for the implementation of planned short-term pollution measurements in the tundra region because of its widespread nature. Moreover, lichens are easy to identify and the thalli of this species are abundant; lichens form a significant element of the tundra region as the beginning of the food chain in the Arctic ecosystems. However, no information on the life expectancy in natural conditions is available for these species as well as for other fruticose species such as *F. nivalis* or *Cladonia mitis*. Correlation of life expectancy with trace element levels in the fruticose lichen may allow planning of monitoring studies while taking into account the actual rate of accumulation per unit time.

Acknowledgments

This research would not have been possible without the specimens of *Cetrariella delisei* from the Calypsostranda region donated to us by the late Professor Florian Święs (Maria Curie-Skłodowska University in Lublin) who conducted botanical studies in this region.

References

1. Arctic Monitoring and Assessment Programme. AMAP assessment 2002: heavy metals in the Arctic. Oslo: Arctic Monitoring and Assessment Programme; 2005.
2. Weinbruch S, Wiesemann D, Ebert M, Schütze K, Kallenborn R, Stroem J. Chemical composition and sources of aerosol particles at Zeppelin Mountain (Ny-Ålesund, Svalbard): an electron microscopy study. Atmos Environ. 2012;49:142–150. https://doi.org/10.1016/j.atmosenv.2011.12.008
3. Shaw GE. The Arctic haze phenomenon. Bull Am Meteorol Soc. 1995;76(12):2403–2413. https://doi.org/10.1175/1520-0477(1995)076<2403:TAHP>2.0.CO;2
4. Nriagu JO. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. Nature. 1979;279:409–411. https://doi.org/10.1038/279409a0
5. Nriagu JO. A global assessment of natural sources of atmospheric trace metals. Nature. 1989;338(6210):47–49. https://doi.org/10.1038/338047a0
6. Ruman M, Kozak K, Lehmann S, Kozioł K, Polkowska Z. Pollutants present in different components of the Svalbard archipelago environment. Ecological Chemistry and Engineering S. 2012;19(4):571–584. https://doi.org/10.2478/v10216-011-0040-9
7. Samecka-Cymerman A, Wojtuń B, Kolon K, Kempers AJ. *Sanionia uncinata* (Hedw.) Loeske as bioindicator of metal pollution in polar regions. Polar Biol. 2011;34(3):381–388. https://doi.org/10.1007/s00300-010-0893-x
8. Riget FU, Asmund G, Aastrup P. The use of lichen (*Cetrariella nivalis*) and moss (*Rhacomitrium lanuginosum*) as monitors for atmospheric deposition in Greenland. Sci Total Environ. 2000;245(1–3):137–148. https://doi.org/10.1016/S0048-9697(99)00439-8
9. Steinnes E. A critical evaluation of the use of naturally growing moss to monitor the deposition of atmospheric metals. Sci Total Environ. 1995;160:243–249. https://doi.org/10.1016/0048-9697(95)04360-D
10. Drbal K, Elster J, Komarek J. Heavy metals in water, ice and biological material from Spitsbergen, Svalbard. Polar Res. 1992;11(2):99–101. https://doi.org/10.3402/polar.v11i2.6721
11. Węgrzyn M, Wietrzyk P, Lisowska M, Klimek B, Nicia P. What influences heavy metals accumulation in arctic lichen *Cetrariella delisei* in Svalbard? Polar Sci. 2016;10(4):532–540. https://doi.org/10.1016/j.polar.2016.10.002
12. Garty J. Biomonitoring atmospheric heavy metals with lichens: theory and application. CRC Crit Rev Plant Sci. 2001;20(4):309–371. https://doi.org/10.1080/20013591099254
13. Węgrzyn M, Lisowska M, Nicia P. The value of the terricolous lichen *Cetrariella delisei* in the biomonitoring of heavy metal concentrations in Svalbard. Pol Polar Res. 2013;34(4):375–382. https://doi.org/10.2478/popore-2013-0022
14. van der Wal R, van Lieshout SMJ, Loonen MJJE. Differential effects of reindeer on high Arctic lichens. J Veg Sci. 2001;12:705–710. https://doi.org/10.2307/3236911
15. Ziaja W, Dudek J, Lisowska M, Olech M, Ostafin K, Osyczka P, et al. Western Sørkapp Land natural environment transformation since the 1980s. Krakow: Jagiellonian University Press; 2011.
16. Joly K, Jandt RR, Klein DR. Decrease of lichens in Arctic ecosystems: the role of wildfire, caribou, reindeer, competition and climate in north-western Alaska. Polar Res. 2009;28:433–442. https://doi.org/10.1111/j.1751-8369.2009.00113.x
17. Allen-Gil SM, Ford J, Lasorsa BK, Monetti M, Vlasova T, Landers DH. Heavy metal contamination in the Taimyr Peninsula, Siberian Arctic. Sci Total Environ. 2003;301:119–138. https://doi.org/10.1016/S0048-9697(02)00295-4
18. Naeth MA, Wilkinson SR. Lichens as biomonitors of air quality around a diamond mine, Northwest Territories, Canada. J Environ Qual. 2008;37(5):1675–1684. https://doi.org/10.2134/jeq2007.0090
19. Sødergaard J, Johansen P, Asmund G, Rigét F. Trends of lead and zinc in resident and transplanted *Flavocetraria nivalis* lichens near a former lead–zinc mine in West Greenland. Sci Total Environ. 2011;409:4063–4071.

https://doi.org/10.1016/j.scitotenv.2011.06.054

20. Zhulidov AV, Robarts RD, Pavlov DF, Kämäri J, Gurtovaya TY, Meriläinen JJ, et al. Long-term changes of heavy metal and sulphur concentrations in ecosystems of the Taymyr Peninsula (Russian Federation) north of the Norilsk Industrial Complex. Environ Monit Assess. 2011;181:539–553. https://doi.org/10.1007/s10661-010-1848-y
21. Melke J, Uziak S. Heavy metals in soils and vascular plants of the Bellsund area (Spitsbergen). Polish Journal of Soil Science. 2006;34(2):20–33.
22. Jóźwik Z. Heavy metals in tundra plants of Bellsund area, Spitsbergen. Pol Polar Res. 1990;11:401–409
23. Jóźwik Z. Heavy metals in tundra plants of the Bellsund in West Spitsbergen, investigated in the years 1987–1995. Pol Polar Res. 2000;21:43–54.
24. Grodzinska K, Godzik B. Heavy metals and sulphur in mosses from southern Spitsbergen. Polar Res. 1991;9(2):133–140. https://doi.org/10.3402/polar.v9i2.6786
25. Wojtuń B, Samecka-Cymerman A, Kolon K, Kempers AJ, Skrzypek G. Metals in some dominant vascular plants, mosses, lichens, algae, and the biological soil crust in various types of terrestrial tundra, SW Spitsbergen, Norway. Polar Biol. 2013;36(12):1799–1809. https://doi.org/10.1007/s00300-013-1399-0
26. Sirois A, Barrie LA. Arctic lower tropospheric aerosol trends and composition at Alert, Canada: 1980–1995. J Geophys Res Atmos. 1999;104(D9):11599–11618. https://doi.org/10.1029/1999JD900077
27. Sastre J, Sahuquillo A, Vidal M, Rauret G. Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction. Anal Chim Acta. 2002;462(1):59–72. https://doi.org/10.1016/S0003-2670(02)00307-0
28. STATISTICA (Data Analysis Software System). Version 10. Tulsa, OK: Statsoft Inc; 2011.
29. Berg T, Kallenborn R, Manø S. Temporal trends in atmospheric heavy metal and organochlorine concentrations at Zeppelin, Svalbard. Arct Antarct Alp Res. 2004;36(3):284–291. https://doi.org/10.1657/1523-0430(2004)036[0284:TTIAHM]2.0.CO;2
30. Garty J. Biomonitoring atmospheric heavy metals with lichens: theory and application. CRC Crit Rev Plant Sci. 2001;20(4):309–371. https://doi.org/10.1080/20013591099254
31. Hestmark G, Skogesal O, Skullerud Ø. Growth, population density and population structure of *Cetraria nivalis* during 240 years of primary colonization. Lichenologist. 2005;37(6):535–541. https://doi.org/10.1017/S0024282905014891
32. Beckett RP, Brown DH. The control of cadmium uptake in the lichen genus *Peltigera*. J Exp Bot. 1984;35:1071–1082. https://doi.org/10.1093/jxb/35.7.1071
33. Brown DH. Mineral uptake by lichens. In: Brown DH, Hawksworth DL, Bailey RH, editors. Lichenology: progress and problems. London: Academic Press; 1976. p. 419–439.
34. Nieboer E, Richardson DHS, Tomassini FD. Mineral uptake and release by lichens: an overview. Bryologist. 1978;81:226–245. https://doi.org/10.2307/3242185
35. Garty J, Galun M, Kessel M. Localization of heavy metals and other elements accumulated in the lichen thallus. New Phytol. 1979;82:159–168. https://doi.org/10.1111/j.1469-8137.1979.tb07571.x
36. Bačkor M, Loppi S. Interactions of lichens with heavy metals. Biol Plant. 2009;53(2):214–222. https://doi.org/10.1007/s10535-009-0042-y
37. Brown DH. The location of mineral elements in lichens: implications for metabolism. In: Peveling E, editor. Progress and problems in lichenology in the eighties. Berlin: Cramer; 1987. p. 361–375. (Bibliotheca Lichenologica; vol 25).
38. Osyczka P, Boroń P, Lenart-Boroń A, Rola K. Modifications in the structure of the lichen *Cladonia* thallus in the aftermath of habitat contamination and implications for its heavy-metal accumulation capacity. Environ Sci Pollut Res Int. 2018;25(2):1950–1961. https://doi.org/10.1007/s11356-017-0639-1
39. Purvis OW. The occurrence of copper oxalate in lichens growing on copper sulphide-bearing rocks in Scandinavia. Lichenologist. 1984;16:197–204. https://doi.org/10.1017/S0024282984000347
40. Chisholm JE, Jones GC, Purvis OW. Hydrated copper oxalate, moolooite, in lichens. Mineral Mag. 1987;51(5):715–718. https://doi.org/10.1180/minmag.1987.051.363.12
41. Sarret G, Manceau A, Cuny D, van Haluwyn C, Déruelle S, Hazeman JL, et al.

Mechanisms of lichen resistance to metallic pollution. Environ Sci Technol. 1998;32:3325–3330. https://doi.org/10.1021/es970718n

42. Branquinho C, Catarino F, Brown DH, Pereira MJ, Soares A. Improving the use of lichens as biomonitors of atmospheric metal pollution. Sci Total Environ. 1999;232:67–77. https://doi.org/10.1016/S0048-9697(99)00111-4
43. Monnet F, Bordas F, Deluchat V, Baudu M. Toxicity of copper excess on the lichen *Dermatocarpon luridum*: antioxidant enzyme activities. Chemosphere. 2006;65:1806–1813. https://doi.org/10.1016/j.chemosphere.2006.04.022
44. Walther DA, Ramelov GJ, Beck JN, Young JC, Callahan JD, Marcon MF. Temporal changes in metal levels of the lichen *Parmotrema praesorediosum* and *Ramalina stenospora*, southwest Louisiana. Water Air Soil Pollut. 1990;53:189–200. https://doi.org/10.1007/BF00155003
45. Azcue J, Mudroch A. Comparison of different washing, ashing, and digestion methods for the analysis of trace elements in vegetation. Int J Environ Anal Chem. 1994;57(2):151–162. https://doi.org/10.1080/03067319408027420
46. Avango D, Hacquebord L, Aalders Y, de Haas H, Gustafsson U, Kruse F. Between markets and geo-politics: natural resource exploitation on Spitsbergen from 1600 to the present day. Polar Rec. 2001;47(1):29–39. https://doi.org/10.1017/S0032247410000069